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Properties of Internally Oxidized Columbium-Zirconium Alloy

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Figure 1. The variation in lattice parameter of Cb-1.6%Zr alloy with increasing oxygen content.

Figure 2. Electron transmission photomicrograph of Cb-1.6%Zr alloy containing 1.0 atomic percent oxygen. X20,000

Figure 3. The variation of ultimate tensile strength, 0.2% offset yield strength and microhardness of Cb-1.6%Zr alloy with increasing oxygen content.

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Introduction

The alloy of columbium with 1% zirconium is one of the most widely investigated columbium alloys. One direction the investigations have taken is to study the influence of interstitial impurities upon the properties of the alloy. Since the amount of impurities generally found in commercial alloys range from a few parts per million to a few hundred parts per million, most studies have been concerned with this range of interstitial impurities and particularly of oxygen. Recently however, columbium-zirconium alloys with higher oxygen content have been investigated.

Hobson (1) studied the lattice parameter of columbium 0.88% zirconium alloys with varying amounts of oxygen. His alloys were annealed at 1600°C and rapidly cooled. He found that the lattice parameter increased to a maximum value at an oxygen content of 300 ppm and decreased at higher oxygen contents. Hobson explained this behavior by assuming that the maximum solid solubility of oxygen in the columbium-0.88% Zirconium alloy at 1600°C is 300 ppm. At higher oxygen content the solubility product for zirconium and oxygen in columbium is exceeded and zirconium oxide is precipitated. Since both zirconium and oxygen in solution increase the lattice parameter of columbium, the removal of these elements from solid solution as precipitate causes the lattice parameter to decrease.

Assuming that the solubility of oxygen in the columbium-zirconium alloy should increase with increasing temperature, Hobson argued that this should make the ternary alloys susceptible to age hardening. Hobson was indeed able to age harden columbium-zirconium-oxygen alloys by quenching them from solutionizing temperatures of 1600, 1800 and 2000°C and age harden them subsequently, provided their oxygen content was low enough so that no second phase was present at the solutionizing temperature. In this way, Hobson determined the maximum solid solubility of oxygen in the columbium-0.88% zirconium alloy to be 300 ppm at 1600°C, between 700 and 800 ppm at 1800°C and more than 950 ppm at 2000°C.

Other work reported on the solubility of oxygen in this alloy system is that of Barber and Morton (2). They reported the solubility of oxygen in Cb-1%Zr alloy at 1000°C to be less than 50 ppm. Cooke's calculations as reported by Pollock (3) show that for Cb-Zr alloy system the solubility limit of oxygen decreases not only with decreasing annealing temperature, but also with increasing zirconium content. His calculations show that the solubility limit in Cb-1%Zr alloy at 1250°C is about 60 ppm while at 1000°C it is less than 50 ppm.

In this investigation the effect of oxygen on the lattice parameter of a columbium-zirconium alloy was studied, over a wider range of oxygen content than has been done before.

In addition the microstructure and the mechanical properties of the alloy high in oxygen were determined. The alloy selected was a Cb-1.0% nominal Zr alloy. However, a chemical analysis showed that it actually contained 1.6% zirconium.

Experimental Procedure

A loop of cold rolled strip of the columbium-1.6% zirconium alloy, 9" long, 0.25" wide and 0.002" thick was suspended from platinium electrodes in a vacuum system. The loop could be heated by passing current through it to temperatures measured with an optical pyrometer. The strip was first annealed at 1250°C in a static vacuum of 10^{-6} Torr. It was then internally oxidized at a temperature of 1250°C by heating it in an atmosphere of oxygen. The partial pressure of the oxygen in the known volume of the vacuum system was adjusted to produce alloys with controlled amounts of oxygen. Pressure measurements showed that all of the oxygen in the system reacted with the alloy strip within one minute. In order to obtain an even distribution of the oxygen in the alloy the strip was heated for an additional three minutes, which is ample according to the calculations based on the known diffusivity of oxygen in columbium (4) at the internal oxidation temperature.

The lattice parameter of the alloys were measured with a diffractometer. The tensile strength was determined on an Instron tensile testing machine and the hardness with a kentron micro-hardness tester using a 300 gm load.

Results and Discussion

Figure 1 shows the relationship between the lattice parameter and oxygen content of a Cb-1.6%Zr alloy as found in this investigation; along with that for a Cb-0.88%Zr alloy, which was obtained by Hobson (1).

The initial increase and subsequent decrease in the lattice parameter of the columbium-1.6%zirconium alloy oxidized at 1250°C can be explained in the same manner as the one found by Hobson in his 0.88% zirconium alloy. The increase is due to the effect of oxygen added in solid solution to the alloy. The amount so added without causing precipitation of ZrO_2 is extremely small. As soon as the limit of solid solubility is reached, zirconium oxide is precipitated, lowering the amounts of both zirconium and oxygen left in solution; therefore the lattice parameter decreases.

For higher oxygen contents the slope of the lattice parameter vs oxygen curve decreases continually until a minimum is reached at 3.0 atomic percent oxygen. With still higher oxygen content the lattice parameter increases again slowly up to 3.5 atomic percent oxygen and rapidly thereafter. At the minimum in the curve a large portion of zirconium has precipitated but there is still some zirconium left in solution. In the range between 3.0 and 3.5 atomic percent oxygen, this remaining zirconium is precipitated. Therefore the increase in lattice parameter which would be expected because of the increasing amount of oxygen in solution is partially compensated by the decrease due to zirconium coming out of solution. The rapid increase in the lattice parameter with more than 3.5 atomic percent oxygen is due to the fact that all the additional oxygen goes in to solution.

The fact that the maximum lattice parameter in the alloy series with 1.6% zirconium was observed at an oxygen content of 300 ppm (0.18 atomic percent) should not be interpreted as fixing the solid solubility of oxygen at 1250°C in the 1.6% zirconium alloy at this value. Since in this investigation it was not possible to work with less than 300 ppm of oxygen with any appreciable accuracy, due to apparatus limitations, it is not possible to say exactly where the solubility limit of oxygen at 1250°C lies. Hobson's and Barber and Morton's work along with Cooke's calculations, as mentioned in the introduction, indicate that the dolubility of oxygen in Cb-1.6%Zr alloy at 1250°C should be about 50 ppm.

Hobson calculated the amounts of oxygen and zirconium in solid solution in the ternary alloy on the basis of the mass action law, taking the maximum solid solubility of oxygen in his Cb-0.88%Zr alloys at 1600°C as 300 ppm. He assumed that the activity of the solutes is proportional to their mole-fration. A similar calculation was made for the Cb-1.6%Zr alloy assuming, as Hobson did, that the precipitating phase is ZrO_2. The maximum solubility of oxygen in the Cb-1.6%Zr alloy is taken as 50 ppm. On the basis of this calculation the lattice parameter of the ternary alloys with increasing amounts of oxygen can be calculated, making the assumption that the contributions of zirconium and oxygen in solution to the lattice parameter are additive. The character of the curve for the lattice parameter vs oxygen content so calculated is very similar to the one actually found. However, the absolute values of the lattice parameter observed are considerably lower than would be expected from the calculation. In particular, the lattice parameter at the minimum of the observed curve should still be well above that of pure columbium, because there are still appreciable amounts of zirconium and oxygen in solid solution. As the data in figure 1 show, the lattice parameter of the alloy is actually well below that of pure columbium of 3.3002 Å as determined by Seybolt (5). It must be concluded that there is either an interaction between the zirconium and oxygen atoms in solution in the columbium, an interaction between these dissolved atoms with the second phase particles, an effect of the small particles themselves or a combination of these effects which causes a contraction of the lattice. Hobson found a similar effect. The lattice parameter of his 0.88% alloy containing 2400 ppm of oxygen is also smaller than that of pure columbium.

Microstructure

Because of the very small size it was not possible to resolve precipitate in either optical micrographs or electron micrographs of replicas. The only data obtainable from these micrographs was the grain size of alloys with different amounts of oxygen, which was found to be approximately 20 microns. A transmission electron micrograph of an alloy with 1 atomic percent oxygen is shown in figure 2. Very small second phase particles can be observed. The grains visible in the micrograph which have a diameter of approximately 1 micron are interpreted as subgrains.

Mechanical Properties

Figure 3 shows the effect of increasing oxygen content on the ultimate tensile strength, the 0.2% offset yield strength and the microhardness of the Cb-1.6%Zr alloy. The increase in these properties with increasing oxygen content is believed to be due to the combined effect of oxygen and zirconium in solid solution and the dispersed ZrO_2 particles.

The considerable scatter in the ultimate tensile strength and the yield strength values measured must be attributed to the very small cross section of the samples and the high absolute values of the strength. The scatter becomes more pronounced for the alloys with more than 2 atomic percent oxygen which were quite brittle. It is therefore doubtful if there is really a maximum in tensile strength at about 3.5 atomic percent oxygen as the data seem to indicate.

Acknowledgment

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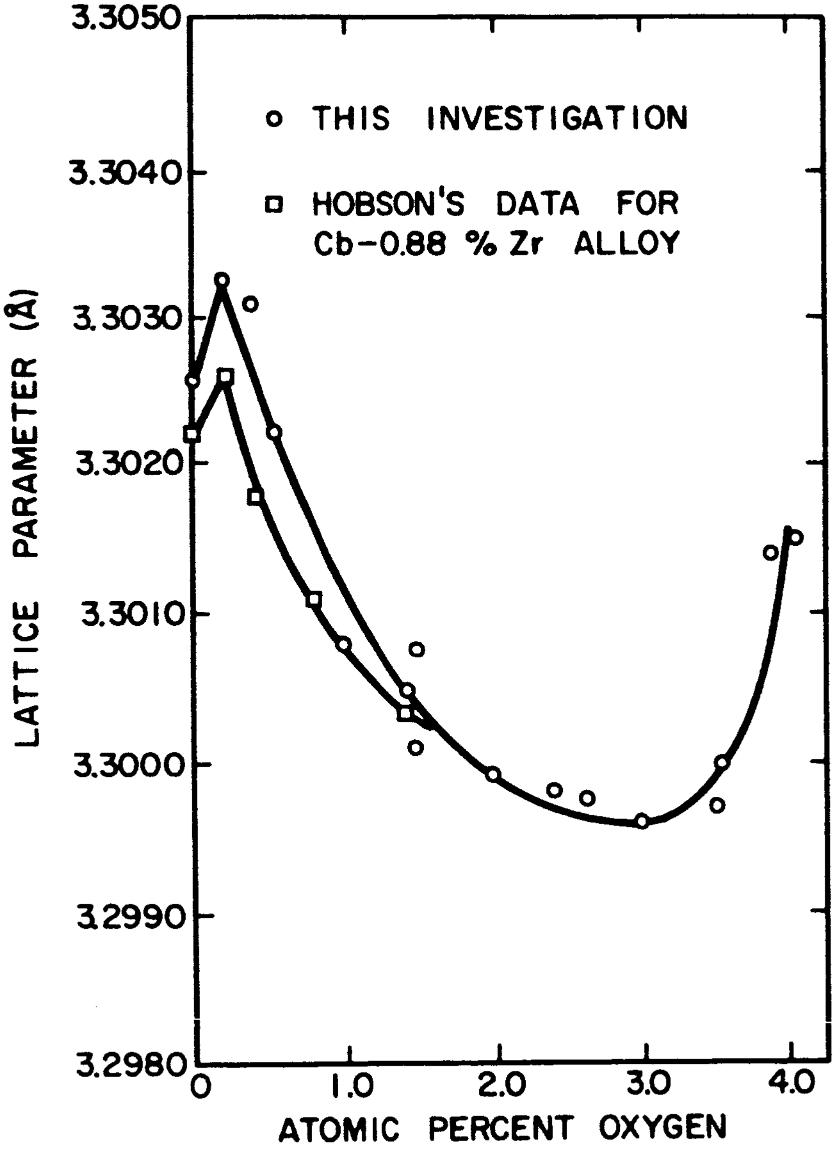
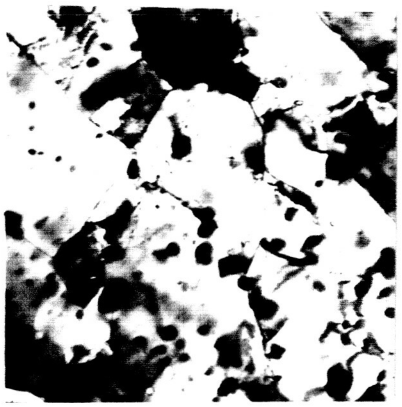
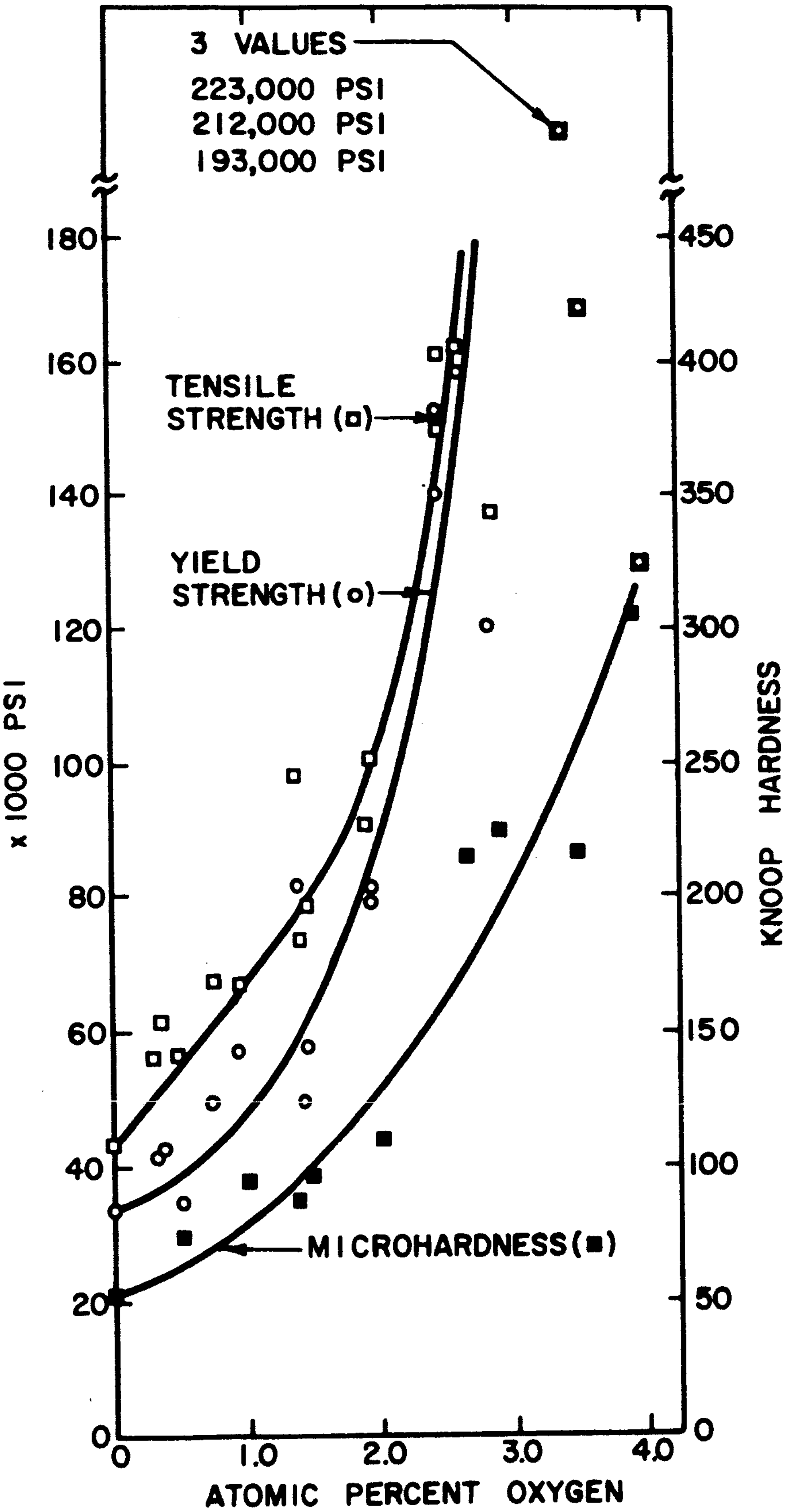


3.3050
3.3040
3.3030
3.3020
3.3010
3.3000
3.2990
3.2980
LATTICE PARAMETER (Å)
o THIS INVESTIGATION
□ HOBSON'S DATA FOR
Cb-0.88 % Zr ALLOY
0
1.0
2.0
3.0
4.0
ATOMIC PERCENT OXYGEN





3 VALUES
223,000 PSI
212,000 PSI
193,000 PSI
TENSILE STRENGTH (□)
YIELD STRENGTH (○)
MICROHARDNESS (■)
x 1000 PSI
KNOOP HARDNESS
ATOMIC PERCENT OXYGEN
0
20
40
60
80
100
120
140
160
180
50
100
150
200
250
300
350
400
450
1.0
2.0
3.0
4.0